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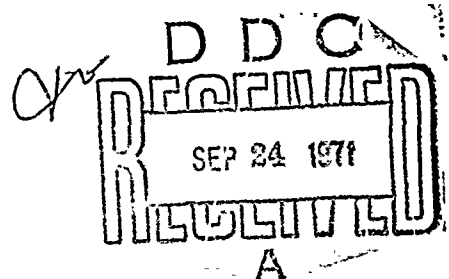
FERROCENE CURING AGENTS (U)

C. LAWRENCE ENNIS, CAPT , USAF

TECHNICAL REPORT AFRPL-TR-71-71

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FERROCENE CURING AGENTS (U)

C. Lawrence Ennis, Capt, USAF

July 1971

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FOREWORD

(U) The author gratefully acknowledges the valuable technical guidance provided by Dr. F.Q. Roberto of the Air Force Rocket Propulsion Laboratory who served as lead scientist on this program. Acknowledgment is also made to Capt C.S. McDowell, PhD, whose inventive flair made the propellant formulating done in this program much safer and much more accurate than would have otherwise been possible.

(U) This work was accomplished under Project 314804ACH and covers the period of 1 July 1969 through 30 June 1970. The Project Scientist was Capt C. Lawrence Ennis.

(U) This technical report has been reviewed and is approved.

CHARLES R. COOKE
Chief, Solid Rocket Division

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CONFIDENTIAL ABSTRACT

(C) With the goal of producing a stable, nonmigrating ferrocene burn rate modifier, four ferrocene diols were examined in the role of curing agents. 1,1'-bis(hydroxymethyl)ferrocene and 1,1'-bis(α -hydroxyethyl)ferrocene were eliminated because of poor physical properties in the gumstocks and propellants obtained from them. 1,1'-bis(γ -hydroxypropyl)ferrocene (BHPF) and 1,1'-bis(δ -hydroxybutyl)ferrocene (BHBF), however, were both found to be excellent curing agents.

(C) Both BHPF and BHBF gave well-cured gumstocks and propellants with the propellant physical properties ranging from 63 to 110 psi tensile strength and 9 to 21 percent elongation. The propellants contained the equivalent of 1.7 to 3.0 percent NBF, but in a form which could not migrate or crystallize, two problems which have plagued NBF.

(C) The burn rate enhancement of both diols is at least equal to NBF based on total iron content. Comparisons were made over a range from 0.6 to 1.0 in./s at 1000 psi.

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GLOSSARY

| | |
|----------|--|
| AP | ammonium perchlorate |
| BHBF | 1, 1'-bis(δ -hydroxybutyl)ferrocene |
| BHEF | 1, 1'-bis(α -hydroxyethyl)ferrocene |
| BHMF | 1, 1'-bis(hydroxymethyl)ferrocene |
| BHPF | 1, 1'-bis(γ -hydroxypropyl)ferrocene |
| CLO | Circo Light Oil (TM) |
| DBF | di-n-butylferrocene |
| DBP | di-n-butyl phthalate |
| DBTDA | di-n-butyltin diacetate |
| HDO | 1, 6-hexamethylenediol |
| LAH | lithium aluminum hydride |
| NAF | n-amylferrocene |
| NBF | n-butylferrocene |
| PTMG-TDI | polytrimethylene glycol end-capped with 2, 4-tolylenediisocyanate |
| THF | tetrahydrofuran |

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SECTION I

INTRODUCTION

(U) Transition metals have been employed as ballistic modifiers in solid propellants since the work of Vogel (Reference 1) in 1951 at the Jet Propulsion Laboratory. Iron Oxide, Fe_2O_3 , was found to be particularly effective and has since been used extensively as a solid additive. Iron oxide is a solid, and its interaction with the other propellant species is a surface phenomenon. Consequently, for greatest efficiency, a large surface area is desirable. This is confirmed experimentally since the efficiency of iron oxide in increasing burn rates improves with smaller particle sizes. The optimum efficiency would be realized if the oxide were present in the monomolecular state but practical problems prevent reduction of solid particles to this region. Because of this phenomenon, the advent of ferrocene caused a significant increase in the efficiency of iron compounds as ballistic modifiers. Oxidation of the ferrocene in the burning propellant produces iron oxide in the desired monomolecular state, and as expected, a given quantity of iron present as ferrocene produces a higher burn rate than an equal quantity of iron as iron oxide.

(U) The use of ferrocene, however, has presented other problems. Since the material is a crystalline solid with a high vapor pressure, it has a marked tendency to migrate through the propellant grain and crystallize at boundary surfaces. Quite obviously this has a deleterious effect on the ballistic properties of the propellant and there has been a considerable effort to eliminate this problem. In 1963, Thiokol (Reference 2) advanced n-butylferrocene (NBF) as an alternative to ferrocene. Since NBF is a liquid, crystallization is no longer a problem, and its action as a plasticizer allows its use in propellants with higher solids loadings. The total percentage of iron, however, is lower than ferrocene, and the tendency to migrate, particularly at elevated temperatures, persists. Further work in the area of ferrocene plasticizers led to the development of significantly better burn-rate modifiers. PLASTISCAT XXI (TM), HYCAT (TM) AND CATOCENE (TM),

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products of Thiokol Chemical Corporation, United Technology Center and Arapahoe Chemical Company, respectively, all represent liquid ferrocene compounds with migratory aptitudes lower than NBF and with approximately the same iron content. But, despite the improvement, at elevated temperatures the migration problem remains. Consequently, a ballistic modifier was still needed which would remain uniformly distributed through the propellant while still retaining its effectiveness as a burn rate modifier.

(U) More recent work has centered on chemically binding the ferrocene derivative to the propellant. The most obvious route is by preparation of a binder which contains ferrocene as an integral part of the polymer. Most attempts to do this have led to polymers with poor physical properties, either solids or plastic materials (Reference 3). Although some liquid copolymers containing ferrocene have been synthesized and cured in gumstocks (Reference 4), there have been difficulties with the physical properties of the propellants prepared from them.

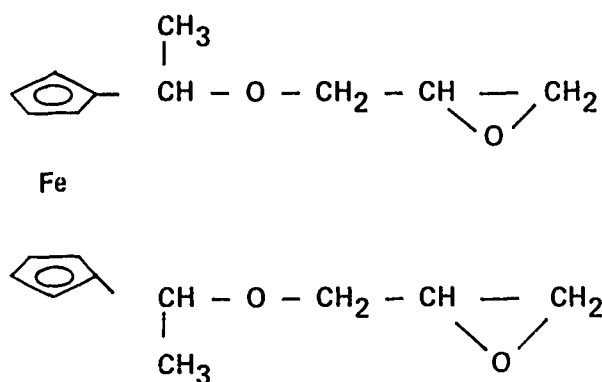
(U) A novel approach to incorporating the ferrocene moiety into a propellant has been examined by Fisher (Reference 5) at Redstone Arsenal. He found that by coating AP with aziridinylmethylferrocene, a 30 percent burn rate increase over propellants with conventional ferrocene modifiers was observed. The method suffers from one main disadvantage: the amount of ferrocene which can be introduced in this fashion is limited. There is also some speculation that the thermal stability of such a propellant may be considerably lowered because of the intimate contact between ferrocene and AP.

(U) An approach which has received only slight attention is the incorporation of the ferrocene as the curing agent. This has the advantage of requiring low molecular weight compounds which are relatively easy to synthesize and purify. The main disadvantage stems from the limited amount of ferrocene which can be incorporated in this fashion. An obvious combination, however, would be a ferrocene curing agent and a polymer

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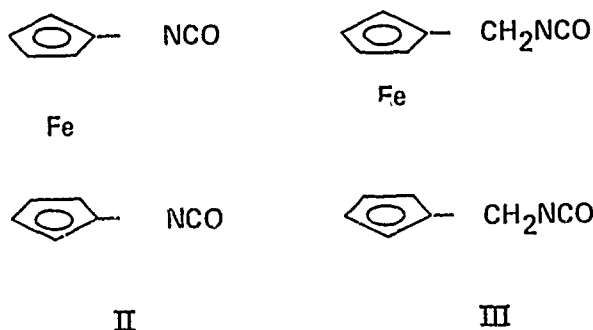
containing only a small amount of ferrocene. Polymers of the latter type do not suffer as seriously from physical property problems as those with high ferrocene content. The combination would then be a binder with a relatively high total iron content. Since the ferrocene is an integral part of the binder in this system, migration problems would be nonexistent. The purpose of this report, therefore, is to describe the results obtained with several new ferrocene curing agents. Preliminary investigation in this area was carried out by Dewey (Reference 3d) of the Air Force Rocket Propulsion Laboratory. He synthesized 1,1'-bis(glycidoxyethyl)ferrocene (I) and cured it with a carboxy-terminated polybutadiene. The result was a rubber with only fair physical properties. Because of time limitations, Dr. Dewey was unable to pursue this system further.



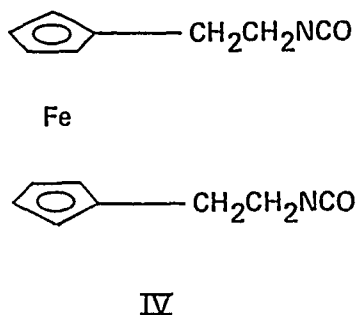
(U) The author chose to examine the isocyanate-alcohol cure system primarily for synthetic reasons. The approach initiated by Dr. Dewey of using heteroannularly disubstituted ferrocenes instead of a monosubstituted ferrocene with a difunctional side chain was continued. Since most curing agents in the urethane system carry the isocyanate functions, ferrocenyl isocyanates were given first consideration. It was felt that the strong inductive effect of the ferrocene group would deactivate 1,1'-diisocyanatoferrocene (II) and even 1,1'-bis(isocyanatomethyl)ferrocene (III) toward

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nucleophilic attack by alcohols. This would be particularly detrimental if they were to be used in combination with the common diisocyanates which are more reactive.



These considerations lead to compounds such as 1,1'-bis(β -isocyanatoethyl)-ferrocene (IV) and those with longer side chains. These compounds become



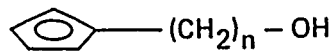
increasingly more difficult to produce synthetically, however, as the functional group is removed from the α -position of the side chain. If, on the other hand, the common functional grouping of the curing agent and prepolymer is reversed, a synthetically feasible series of ferrocenyl alcohols can be visualized. 1,1'-bis(hydroxyethyl) ferrocene (V) is commercially available. Others such as VI, VII and VIII would be more difficult to synthesize again because of removal of the functional group from the α -positions, but in each case, the synthetic route would be shorter than that leading to

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the analogous isocyanate. This approach depends on the availability of isocyanate-terminated prepolymers, and fortunately, some excellent ones are available.



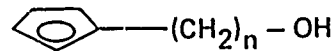
Fe



Fe



V



VI n = 2

VII n = 3

VIII n = 4

(U) Thus, the curing agents examined were V, VII, VIII and 1,1'-bis-(hydroxyethyl)ferrocene (IX), the latter because of its ready availability from 1,1'-diacetylferrocene. These four diols were examined for cure characteristics in gumstocks and propellants. Burn rates, physical properties and other features were also examined and compared with those of conventional curing agents.

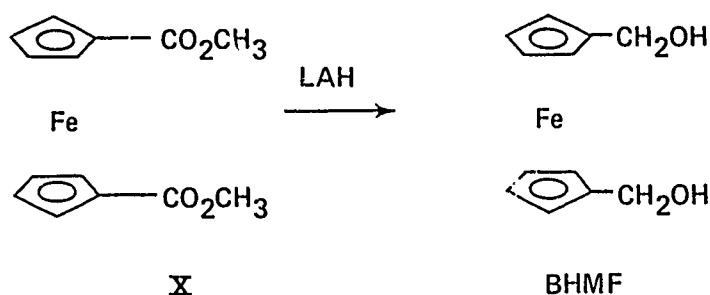
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SECTION II

SYNTHESES OF FERROCENE DIOLS

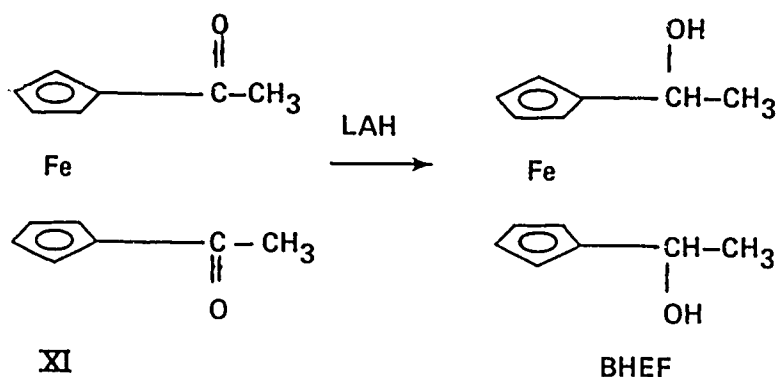
(U) The use of alcohol functions on the ferrocene nucleus is particularly attractive synthetically since reducing conditions, which are frequently required to produce alcohols, do not affect the ferrocene ring. For instance, 1,1'-bis(hydroxymethyl)ferrocene (BHMF)* is readily available from lithium aluminum hydride (LAH) reduction of 1,1'-dicarbomethoxyferrocene (X), which is commercially available at a reasonable price.



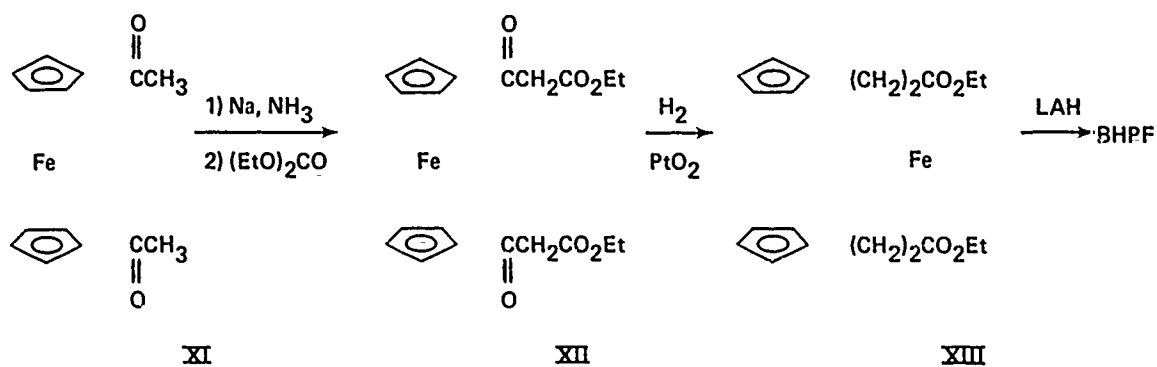
(U) Likewise, BHEF is available from 1,1'-diacetylferrocene (XI). Although this diol does not belong to the homologous series of curing agents of the form $\text{Fc}[(\text{CH}_2)_n\text{OH}]_2$, it was examined because of its availability. As will be shown later, the material is entirely unsatisfactory as a curing agent.

* For reasons of brevity, these curing agents will henceforth be referred to as
BHMF 1,1'-bis(hydroxymethyl)ferrocene, V.
BHEF 1,1'-bis(α -hydroxyethyl)ferrocene, IX.
BHPF 1,1'-bis(γ -hydroxypropyl)ferrocene, VII.
BHBF 1,1'-bis(δ -hydroxybutyl)ferrocene, VIII.

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(U) Syntheses of the two remaining diols involved several steps. BHPF was obtained by reduction of the bis-ester XIII. XIII has been reported (Reference 6) as the product of reduction of the bis keto ester XII which, in



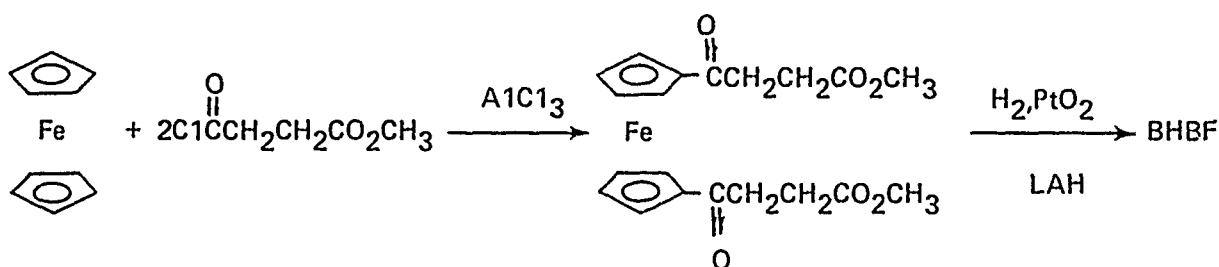
turn, was prepared by carboethoxylation of bisacetylferrocene. Some difficulty was experienced in the hydrogenation of crude XII as reported. If the bis keto-ester was purified before reduction, however, the problems were overcome. BHPF was obtained as an amber oil and was sensitive to light and oxygen as reported previously for alkyl ferrocenes (Reference 7). The diol was quite stable when stored under N_2 in an amber bottle.

(U) The synthetic route to BHBF differed only slightly from that to BHPF. The bis-ketoester XIV was prepared by Friedl-Crafts condensation

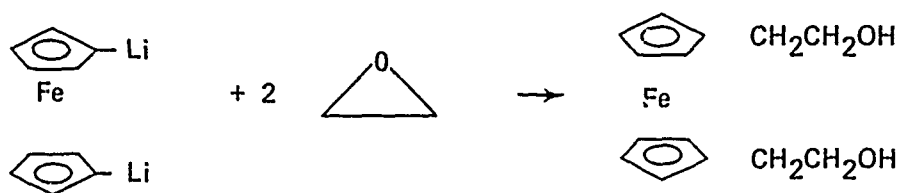
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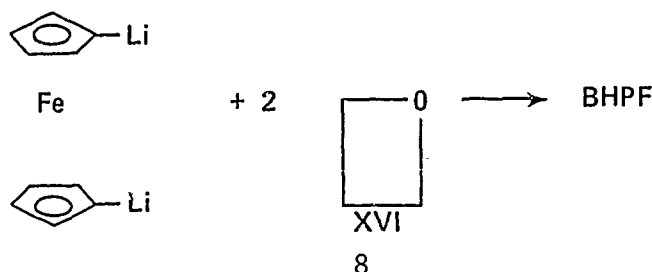
of the appropriate ester-acid chloride with ferrocene, a modification of the procedure reported by Graham, et al. (Reference 8). Again, hydrogenation (Reference 9) followed by LAH reduction gave the diol.



(U) The diol VI ($n = 2$) was not prepared due to time limitations. If the material is a low-melting solid or an oil, it should be an excellent curing agent because of its relatively high iron content. A one-step synthesis has been proposed (Reference 4) in which ethylene oxide is condensed with ferrocenyl dilithium.



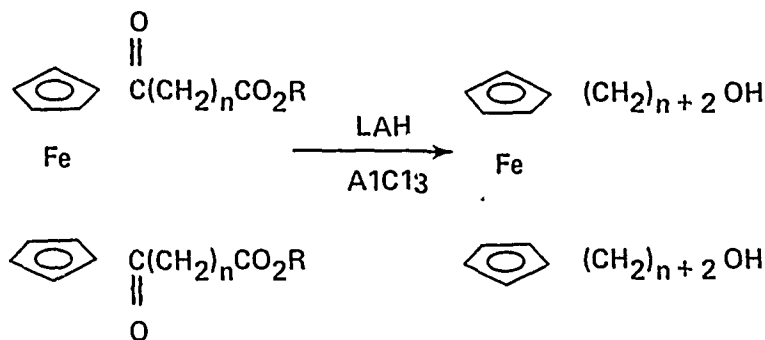
An obvious extension in which oxetane (XVI) is substituted for ethylene oxide may provide a facile route to BHPF.



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(U) The reduction of acylferrocenes to alkylferrocenes using LAH in the presence of aluminum chloride is well known (Reference 10). Application of this reaction to the bis-ketoesters XII and XIV with sufficient LAH to reduce the esters also should provide a direct synthesis of BHPF and BHBF.



XII, $n = 1$, $R = \text{Et}$

XIV, $n = 2$, $R = \text{Me}$

(U) A preliminary examination of this reaction showed that the desired diols were indeed a product of the reaction even though incomplete reduction took place, and a mixture of partially reduced compounds was obtained. Further work on this reaction was precluded by lack of time. Development of this scheme should provide the most facile route to the diols.

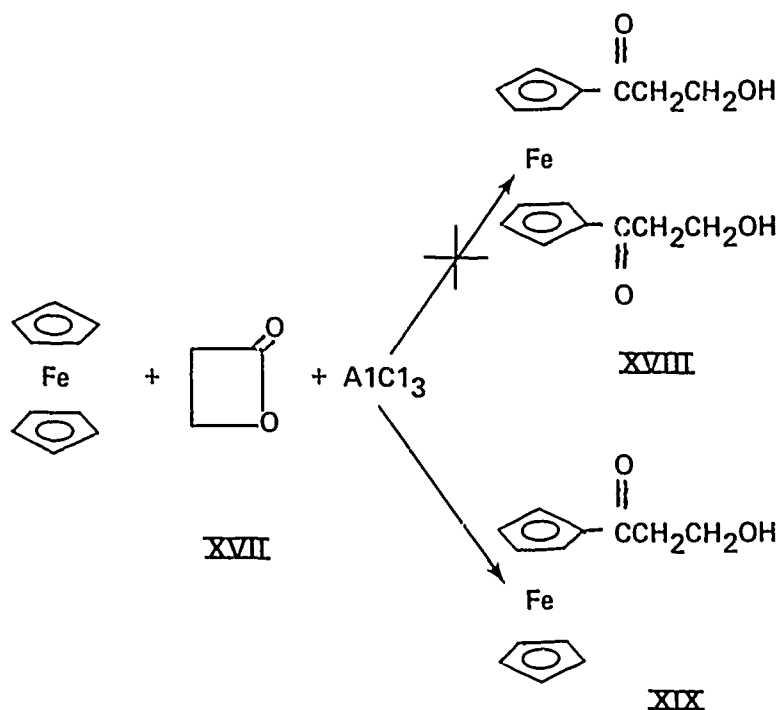
(U) It was mentioned previously that alkylferrocenes are somewhat oxygen and light sensitive. For this reason, ketones of the general

structure $\text{Fc} \left[\begin{array}{c} \text{O} \\ \parallel \\ \text{C}(\text{CH}_2)_n\text{OH} \end{array} \right]_2$ might have a significant advantage over the

bis(hydroxyalkyl)ferrocenes, even though the iron content is somewhat lower.

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A preliminary examination of a synthetic route to 1,1'-bis-(β -hydroxypropionyl)ferrocene (XVIII) was made. Friedl-Crafts condensation of β -propiolactone (XVII) with ferrocene should provide a simple one-step synthesis. When the reaction was carried out, however, only the monosubstituted product (XIX) was obtained.



(U) Time limitations precluded further work in this area, but it is felt that experimental manipulation could force the second substitution to proceed. Extension of this reaction to higher homologs should be simple with the appropriate lactone.

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SECTION III

GUMSTOCKS AND PROPELLANTS

A. GUMSTOCKS

(C) A number of gumstocks were formulated to determine in a qualitative fashion the properties of ferrocene-containing binders. Most of the work on gumstocks utilized BHMF because the amount of curing agent required was relatively large for the information obtained and this material was readily available. Two prepolymers were available which were isocyanate terminated. A polytrimethylene glycol has been end-capped with 2,4-tolylenediisocyanate (PTMG-TDI) by Shell Development to produce a polymer with an equivalent weight of 967 g/eq. The second prepolymer is castor oil (glyceryl triricinoleate) which has also been end-capped with the same diisocyanate by Thiokol Chemical Corporation. This prepolymer, Solithane 113 (TM), has an equivalent weight of 454 g/eq and is essentially trifunctional. The equivalent weight of the polymer is important because it dictates the amount of iron that can be included as the curing agent. A low equivalent weight in the prepolymer calls for a large amount of curing agent and therefore a high iron content. On the other hand, the low equivalent weight generally gives poor physical properties.

(C) BHMF is a solid (mp 105-8°) and is slow to dissolve in either of the prepolymers or the plasticizer (dibutyl phthalate, DBP). For these reasons, special conditions were employed to mix the gumstocks which though not amenable to scale-up were quite useful for laboratory mixes. The prepolymer, the curing agent and the plasticizer were weighed and combined. The mixture was heated to 110°C and stirred until homogeneous, then cooled. This greatly accelerated the cure reaction during the heating period and consequently, decreased the cure time. In the gumstocks, this was of little concern, since after cooling, the samples were simply allowed to cure. With propellants, however, the mix had to be completed quickly because of the greatly reduced pot life. This procedure was found to be generally

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effective for solid curing agents if the temperature employed is slightly above the melting point of the solid.

(C) BHMF is also singular in that it requires no curing catalyst. Apparently, the inductive effect of the ferrocene ring increases the nucleophilicity of the hydroxyl group and consequently, the rate of reaction with the isocyanate group. Fortunately, the pot life of the binder prepared from PTMG-TDI and this diol has a reasonable cure time. The combination of BHMF and Solithane 113, however, has a very short pot life and cures during the cooling process. BHEF, although the hydroxy groups are α to the ring, is a secondary diol and the increase in steric inhibition is sufficient to overcome the inductive effect. This material does require a catalyst to cure in less than 1 day. Likewise, BHPF and BHBF require a cure catalyst.

(C) The first gumstocks were made with the PTMG-TDI prepolymer. Dibutyltin diacetate (DBTDA) was the cure catalyst when one was employed. A formulation (LE34) containing 25 percent DBP with BHMF as curing agent and DBTDA as catalyst cured very fast (within 5 minutes), but gave a rubber with good physical properties. The elongation was well over 1000 percent, even though the sample contained numerous voids introduced during the mixing process. At the same time, the material was quite strong. A gumstock of the same basic binder system but with no plasticizer and without curing agent (LE35) was considerably stronger, but the elongation decreased to 150 percent. Again, the sample contained voids from mixing.

(C) For comparison, two gumstocks were also formulated with 1,6-hexanediol (HDO) as the curing agent. One gumstock (LE36) contained no ferrocene. The other (LE31a) contained sufficient n-amylferrocene (NAF) to give the same iron content as LE34 and LE35. In the latter, the n-amylferrocene replaced the DBP as plasticizer. Both the HDO-cured gumstocks were virtually identical in physical properties to LE34 which was cured with BHMF.

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(C) A gumstock was also prepared using BHEF instead of BHMF. Although the gumstock cured, there were numerous voids present which formed during the curing process. These were thought to be produced by a DBTDA-catalyzed dehydration of the ferrocene diol to a vinyl ferrocene. The water produced in this reaction would react further with the isocyanate present liberating carbon dioxide and causing the voids. For this reason, BHEF was eliminated from further consideration as a curing agent. Table I lists several gumstocks.

B. PROPELLANTS

(U) The ferrocene-cured gumstocks described in the previous section were next examined in a propellant system. Physical properties of propellant samples cured with the various curing agents were tested. Burn rates of these samples were also measured and compared to analogous samples with conventional ferrocene derivatives. And, finally, the solvent properties of the ferrocene-containing gumstocks for other ferrocene derivatives were examined.

(U) All the propellants described in this report were mixed in a McDowell Mixer (Reference 11). This system has the capability of remotely mixing propellants and casting them in the form of straws for strand burning, micro-dog-bones for physical property testing and motors for ballistic testing. In addition, all functions can be carried out under high vacuum (<0.1 mm). The capacity of the mixer is from 1g to 100g with less than 5 percent loss when casting.

(C) 1. Physical Properties. For the purpose of stress-strain measurements, an 80 percent solids level was established. The ingredients consisted of 15 percent Al (200 atm), 65 percent AP consisting of a trimodal blend of particle sizes (18.2 percent 400μ , 44.2 percent 200μ , 37.5 percent 45μ), 5 percent plasticizer and 15 percent binder. All of the samples to be described were cured at 35°C under a nitrogen atmosphere.

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(C) TABLE I. (U) GUMSTOCKS

| | <u>LE34</u> | <u>LE35</u> | <u>LE36</u> | <u>LE36a</u> |
|----------|------------------|------------------|-------------------|-------------------|
| PTMG-TDI | 8.0 g(8.26 meq) | 8.0 g(8.26 meq) | 8.0 g(8.26 meq) | 8.0 g(8.26 meq) |
| BHMF | 1.01 g(8.23 meq) | 1.01 g(8.23 meq) | | |
| HDO | | | 0.486 g(8.23 meq) | 0.486 g(8.23 meq) |
| DBP | 3.0 g | | 3.0 g | 2.0 g |
| NAF | | | | 1.0 g |

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(C) Since the BHMF curing agent with PTMG-TDI gave a tough rubbery gumstock, it was examined first in the propellant system. All samples cured quite well without catalyst but gave brittle propellants with low elongation (Table I). Substitution of Circo Light Oil (TM) for dibutylphthalate (DBP) as plasticizer, gave slightly better elongation (Sample No. LE13), but the oil was only slightly soluble in the binder system. The physical properties of the propellant were relatively insensitive to the OH/NCO ratio* over the range from 0.80 to 1.15 (LE7, LE9, LE11 and LE15, Table II). The low elongation was felt to be a result of the short chain length in the prepolymer. That this is at least partially true will become clear in the remainder of this section. BHMF was not used in a propellant in conjunction with Solithane 113 because of the poor properties of the gumstock. Likewise, BHEF was eliminated in the gumstock phase.

(C) BHPF was examined with PTMG-TDI and Solithane 113. With the former prepolymer, reasonably good properties were observed (LE31), but with Solithane 113, the elongation was again low, resulting in a brittle propellant (LE27). Substitution of Circo Light Oil (TM) for DBP gave even lower elongation (LE21). This was caused by poor solubility of the oil in the binder system, causing bleeding of the plasticizer from the cured propellant grain. A combination of Solithane 113 and PTMG-TDI as expected, gave properties intermediate between the two prepolymers alone when cured with BHPF (LE33). The properties of these propellants are listed in Table III. A propellant cured with BHPF and PTMG-TDI is also described in Table III. Since this propellant has good elongation but low strength, it appears that a combination of BHPF and BHEF with PTMG-TDI will make the best binder system.

*Since the curing agent carries the OH function, the ratio used here is OH/NCO rather than the more common form, NCO/OH.

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(C) TABLE II. (U) PHYSICAL PROPERTIES OF PROPELLANTS
CURED WITH BHMf AND PTMG-TDI

| <u>Sample No.</u> | <u>OH/NCO</u> | <u>Plasticizer</u> | <u>Elongation^a (percent)</u> | <u>Tensile^a (psi)</u> | <u>Modulus^a</u> |
|-------------------|---------------|--------------------|---|--------------------------------------|----------------------------|
| LE15 | 0.8 | DBP | 2 | 133 | 8040 |
| LE11 | 0.95 | DBP | 2 | 121 | 5630 |
| LE7 | 1.05 | DBP | 2 | 138 | 8480 |
| LE9 | 1.15 | DBP | 2 | 146 | 8990 |
| LE13 | 1.05 | CLO ^b | 3 | 180 | 7140 |

^a Average of two samples

^b Circo Light Oil

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(C) TABLE III. (U) PHYSICAL PROPERTIES OF PROPELLANTS
CURED WITH BHPF AND BHPF AS CURING AGENTS
AND PTMG-TDI AND SOLITHANE 113
AS PREPOLYMERS

| Sample No. | Curing Agent | Prepolymer | Plasti- cizer | OH/NCO | Elongation (percent) | Tensile (psi) | Modulus |
|-------------------|-----------------|--|------------------|--------|-------------------------|------------------|---------|
| LE31 ^a | BHPF | PTMG-TDI | DBP | 1.05 | 9 | 108 | 1,500 |
| LE27 ^b | BHPF | Solithane 113 | DBP | 1.05 | 4 | 233 | 7,000 |
| LE21 ^a | BHPF | Solithane 113 | CLO ^d | 1.05 | 2 | 535 | 25,000 |
| LE33 ^a | BHPF | PTMG-TDI & Solithane 113 ^c | DBP | 1.05 | 4 | 153 | 3,800 |
| LE12 ^a | BHPF | PTMG-TDI | DBP | 1.05 | 21 | 63 | 592 |

^a Average of two samples

^b One Sample only

^c 1:1 mixture by No. of Meq.

^d Circo Light Oil (TM)

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(U) These samples were tested as an indication of the physical properties for these types of binders and no further attempt was made to improve the properties.

(U) 2. Burn Rates. To compare the efficiency of the new ferrocene curing agents with conventional ferrocene modifiers, a series of strand burn rates were measured using 3.5-inch strands cast in plastic straws. The burn rates were all measured over a 3-inch section at a pressure of 1000 psi.

(C) Since iron apparently promotes the decomposition of AP and has relatively little effect on the binder or other propellant ingredients, inclusion of the ferrocene moiety into the polymer backbone should not change its catalytic efficiency. To confirm this, propellant formulations were prepared using BHMF as curing agent and burn rate modifier. The burn rates of these mixes were then compared to propellants cured with HDO with sufficient ferrocene plasticizers added to give all samples the same total iron content. This comparison should reveal any differences associated with the form in which the ferrocene group is present. In the first burn rate samples, the formulation used to prepare physical property specimens was duplicated. This consisted of an 80 percent solids loading with 15 percent Al (200 atm), 65 percent AP (trimodal, see page 13), 5 percent plasticizer and 15 percent binder. When a ferrocene plasticizer was employed, it was simply substituted on a weight basis for DBP. The iron content of the first two samples was dictated by the amount of ferrocene curing agent required to give an OH/NCO ratio of 1.05. This was found to be 0.403 percent Fe when BHMF was curing agent, so sufficient di-n-butylferrocene (DBF) was substituted for DBP in the sample cured with HDO to give 0.403 percent Fe also. (This is equivalent to 1.75 percent NBF.) The burn rate of the BHMF-cured propellant (LE42a, 0.48 in./s) was slightly higher than the sample cured with HDO (LE 42c and d, 0.430 in./s), thus confirming our previous hypothesis on the efficiency of ferrocene curing agents.

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(C) In the next series, the same comparison was made but at a 3 percent total Fe content. (This corresponds to 13 percent NBF.) To maintain the same binder level (15 percent) and still add sufficient ferrocene plasticizer to reach 3 percent total Fe, it was necessary to lower the solids loading to 73.5 percent. Although this would be unacceptable for ballistic purposes, it was hoped that any burn rate differences between propellants with the ferrocene curing agents and those with ferrocene plasticizers would be magnified at such a high Fe content. For the propellant cured with BHMF (LE3), it was necessary to add 2.6 percent Fe as DBF to give a total of 3.0 percent; for the HDO-cured propellant (LE2), all of the Fe was present as DBF. The burn rates differed even less in this case; LE3 gave 0.618 in./s and LE2 gave 0.596 in./s. All four of the aforementioned propellants are described in Table IV.

(C) TABLE IV. (U) BURN RATES OF PROPELLANTS
CURED WITH BHMF AND HDO AND
CONTAINING TRIMODAL AP

| <u>Sample No.</u> | <u>Curing Agent</u> | <u>Fe (percent)</u> | <u>r_b^a (in./s)</u> |
|-------------------|---------------------|---------------------|-----------------------------------|
| LE42a | BHMF | 0.403 | 0.476 ^b |
| LE42c and d | HDO | 0.403 | 0.430 ^c |
| LE3 | BHMF | 3.00 | 0.618 ^d |
| LE2 | HDO | 3.00 | 0.596 ^e |

^a At 1000 psi and room temperature

^b Average of three samples

^c Average of eight samples

^d Average of nine samples

^e Average of four samples

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(C) For a comparison of burn rates in the range of 1 in./sec, the next series employed AP with smaller particle sizes. The formulations involved in the four samples described above were used again, but the AP consisted of a bimodal blend of 80 percent 5 μ and 20 percent 45 μ , and the Al was H100. BHBF was also substituted for BHMF. At the 3 percent Fe level, the difference was almost negligible (LE8 and 16, 1.27 in./s and LE10, 1.23 in./s), and at the 0.4 percent Fe level, the burn rates were again virtually the same (LE18, 0.855 in./s and LE17, 0.850 in./s). These samples are described in Table V. Thus, we conclude that the ferrocene curing agents are at least as efficient as the conventional ferrocene plasticizers.

(C) TABLE V. (U) BURN RATE OF PROPELLANTS
CURED WITH BHBF AND HDO AND
CONTAINING BIMODAL AP

| <u>Sample No.</u> | <u>Curing Agent</u> | <u>Fe (percent)</u> | <u>r_b^a (in./s)</u> |
|-------------------|---------------------|---------------------|-----------------------------------|
| LE8 and 16 | BHBF | 3.00 | 1.27 ^b |
| LE10 | HDO | 3.00 | 1.23 ^b |
| LE18 | BHBF | 0.386 | 0.86 ^c |
| LE17 | HDO | 0.386 | 0.85 ^b |

^aAt 1000 psi and room temperature

^bAverage of three samples

^cAverage of four samples

(C) An examination of the burn rate of propellant strands cured with BHMF indicated that its behavior, as expected, is very similar to BHMF and BHBF, differing only in Fe content. A formulation using the bimodal

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blend of AP (5 to 45 μ) and H100 Al with 0.422 percent total Fe* gave a burn rate of 0.90 in./s (compare with LE18, 0.86 in./s, at 0.386 percent Fe). A formulation was also mixed with Solithane 113 as the prepolymer. Because of the lower equivalent weight (454 g/eq), a larger quantity of curing agent is required resulting in a higher total iron content. At an OH/NCO ratio of 1.05 giving an Fe content of 0.720 percent (equivalent to 3.1 percent NBF), a burn rate of 0.98 in./s was measured. Table VI describes these two samples.

(C) TABLE VI. (U) BURN RATES OF PROPELLANTS CURED WITH BHPF

| <u>Sample No.</u> | <u>Binder</u> | <u>Fe (percent)</u> | <u>r_b (in./s)^a</u> |
|-------------------|---------------|---------------------|---|
| LE30 | PTMG-TDI | 0.422 | 0.90 |
| LE35 | Solithane 113 | 0.720 | 0.98 |

^aAt 1000 psi and room temperature

(C) These burn rates do not by any means represent the maximum available with these ferrocene curing agents. Smaller particle size AP (especially ultra-fine AP) and higher solids loadings would both greatly increase r_b . Rather, the intent of these measurements is to illustrate that these modifiers are as effective as conventional ferrocene derivatives and to give some indication of the Fe content available with this type of curing agent. If these ferrocene diols could be used in conjunction with ferrocene-containing prepolymers, even higher iron contents could be realized. Unfortunately, such polymers are not yet available.

*This Fe content is a reflection of the slightly higher iron content of BHPF over BMBF and an OH/NCO ratio of 1.14.

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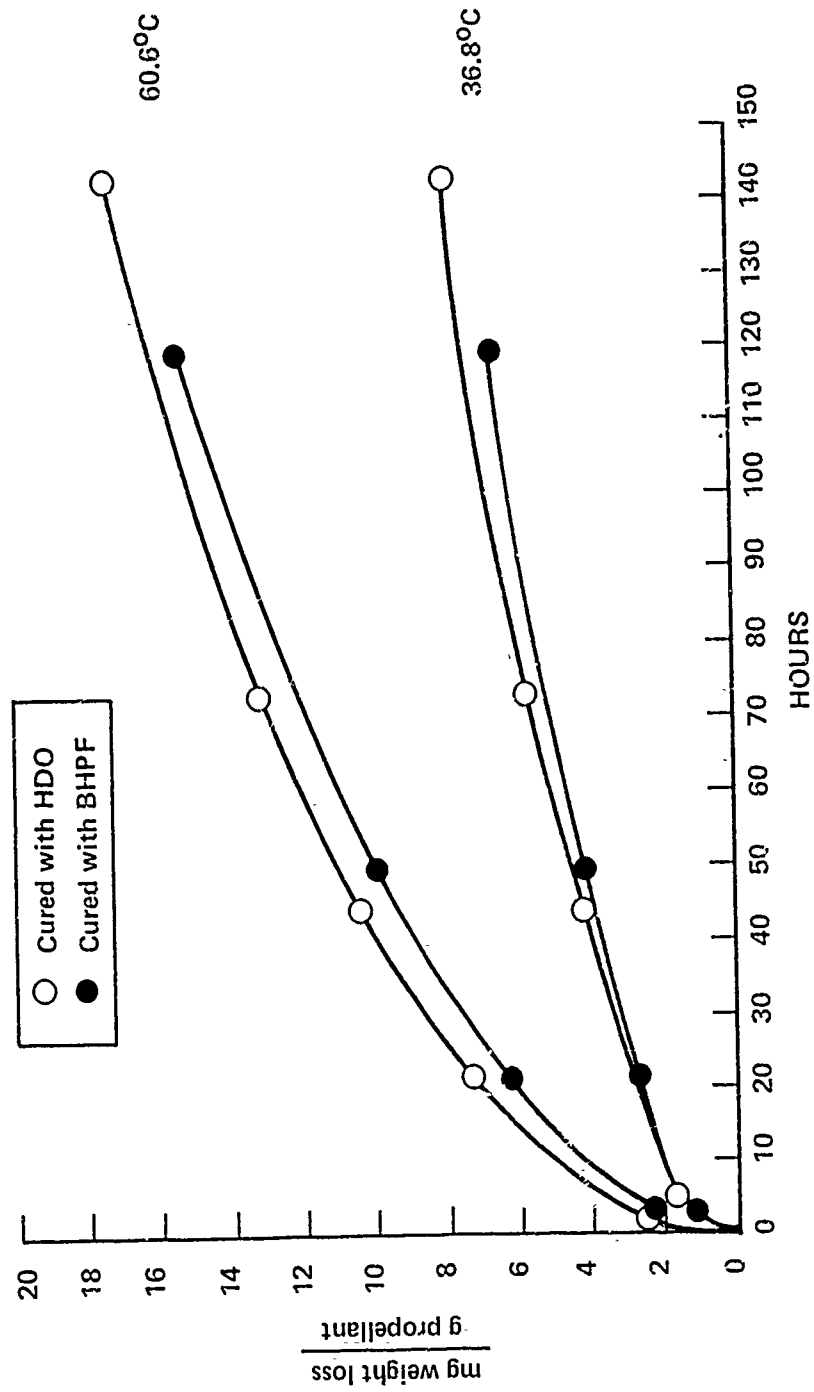
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(U) 3. Solvent Properties of Ferrocene-Containing Propellants

In the past decade, a number of good ferrocene plasticizers have appeared but none has completely solved the problem of migration in a cured propellant. This problem is caused by the fact that a cured solid propellant grain is a very poor solvent system. If the solvent properties of the propellant could be improved, then perhaps a dramatic decrease in migration tendency would be realized. According to solution theory, the best solvent for a particular solute will be the one which most resembles that solute. Therefore, the best solvent system for a ferrocene plasticizer would be a system which also contained ferrocene. We would then predict that a propellant cured with a ferrocene curing agent would be a better solvent system for ferrocene plasticizers than a propellant cured with a conventional diol. If this is true, the result should be a decrease in migration tendency for ferrocene plasticizers in the ferrocene-containing propellant matrix.

(C) To test this hypothesis, two propellant samples were formulated containing 3 percent NBF. One propellant was cured with HDO and one with BHPF. If the ferrocene-containing binder is a significantly better solvent system, it should be reflected in the relative weight losses of the two samples. Accordingly, four specimens of each sample were cut in cube shape, roughly 0.5 g each. Two specimens of each sample were thermostated at 36.8°C and the remainder at 60.6°C under nitrogen atmospheres. Weight loss was followed by weighing the specimens at various time intervals. The results are shown in Figure 1. From the graph, it is obvious that the improvement is only slight. The results, however, could be quite different with a plasticizer such as PXXI which has low migration tendencies to begin with. The slight difference could then become significant. Time limitations precluded such a long-term surveillance under this program.

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(C) Figure 1. (U) Weight Loss versus Time for NBF-Containing Propellants Cured With BHPF and HDO

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(U) Because of the necessary limitations placed on this program, there were a number of items of interest which appeared but could not be pursued. Therefore, in the interest of encouraging further work in this area, I would like to outline several of these items.

(U) As mentioned earlier, the synthesis of BHPF and BHBF could perhaps be greatly simplified by a condensation of oxirane or oxetane with ferrocenyl dilithium. This reaction could be generalized to include condensation with lactones which would lead to ω -hydroxyalkanoylferrocenes. These would be of considerable interest for stability reasons.

(C) From the results of this program, the best curing agent for the polymers available would be a combination of BHPF and BHBF. Perhaps with a tailored polymer, however, such as $\text{OCN}-(\text{CH}_2)_n-\text{NCO}$, BHMF could be used to advantage and n could be adjusted to give the best tradeoff between physical properties and iron content. This polymer could be readily synthesized from available carboxy-terminated polybutadienes and would not contain the relatively large and rigid end group that is present in TDI end-capped polymers. Another possibility would be a combination of BHPF or BHBF with a ferrocene-containing polymer. This is an obvious route to a high total iron content. The solvent property of such systems should be reinvestigated in detail. Perhaps the small effect noted with NBF would be significantly greater if the liquid additive had a low migration tendency to begin with such as P-XXI or catocene.

(C) Despite the amount of work that is obviously needed in this area, it is apparent that incorporation of the ferrocene catalyst into the binder is feasible. Physical properties and iron content could be readily adjusted to meet propellant requirements without the problems introduced with available ferrocene plasticizers.

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SECTION IV

SUMMARY AND CONCLUSIONS

(C) Four heteroannularly disubstituted ferrocene diols have been prepared and evaluated as curing agents. 1,1'-bis(hydroxymethyl)ferrocene (BHMF) and 1,1'-bis(α -hydroxyethyl)ferrocene (BHEF) have been reported in the literature. 1,1'-bis(γ -hydroxypropyl)ferrocene (BHPF) and 1,1'-bis(δ -hydroxybutyl)ferrocene (BHBF) were synthesized and characterized on this program. The cure characteristics of all four curing agents were examined with two isocyanate-terminated prepolymers, PTMG-TDI and Solithane 113.

(C) The diols were cured first in gumstocks then in propellants. BHMF, while useful on a laboratory scale, was not amenable in scale-up because of its high melting point, its poor physical properties in propellants and its short pot life. BHEF was eliminated from further consideration at the gumstock stage because of a competing side reaction. Elimination of water to form vinyl side chains is facile in BHEF in the presence of cure catalysts. The water reacts further with the isocyanates present, generating carbon dioxide and resulting in spongy gumstocks.

(C) BHPF and BHBF are both oils and cure well in both prepolymers. Although the propellants containing these curing agents contain slightly less total iron than those cured with BHMF or BHEF, the physical properties are considerably better. With PTMG-TDI, the properties range from 60 to 110 psi for maximum tensile strength and 10 to 20 percent elongation. At an 80 percent solids level and using 5 percent inert plasticizer, the total iron content that can be introduced in the form of a curing agent is from 0.4 to 0.7 percent, depending upon the equivalent weight of the prepolymer. This is equivalent to a range of 1.75 to 3.0 percent NBF. The obvious advantage of the curing agent approach over NBF is that the curing agents cannot migrate or evaporate.

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(C) The burn rate enhancement of each of the ferrocene diols is at least equal to NBF based on Fe content. Although high burn rates (>1.5 ips at 1000 psi) were not investigated on this program, a rate of 1.0 ips at 1000 psi was easily achieved at only an 80 percent solids level using inert plasticizer and relatively large oxidizer particle size.

(C) The solvent properties of the BHPF and PTMG-TDI binder system for NBF were also examined. The weight loss of propellant samples, however, showed that NBF was lost from this type of binder at a rate only slightly less than that of a propellant cured with hexanediol and PTMG-TDI.

(C) Thus, BHPF and BHBF have been shown to be effective curing agents for isocyanate-terminated prepolymers. A significant iron concentration can be obtained by using only the curing agents as modifiers in a form which has none of the problems of migration, volatilization and crystallization usually attributed to ferrocene derivatives.

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SECTION V EXPERIMENTAL

GENERAL

(U) Infrared spectra were obtained from a Beckman IR-5A. Analyses were carried out by the Analytical Section of the Chemical and Materials Branch, Propellant Division, AFRPL. All thin-layer chromatography was performed on Mallinckrodt ChromAR Sheet 500 (TM). Melting points were taken on a Fisher-Johns Melting Point Apparatus and are uncorrected.

(U) 1, 1'-bis(hydroxymethyl)ferrocene (BHMF)

(U) This material was prepared from the diester by reduction with LAH according to Nesmeyanov (Reference 12). The first crop of crystals (67 percent yield) with a melting point of 105-8°C was used.

(U) 1, 1'-bis(α -hydroxyethyl)ferrocene (BHEF)

(U) A sample of this diol was prepared by F.M. Dewey by LAH reduction of 1, 1'-diacetylferrocene according to Mashburn (Reference 13). The material melted at 58-61°C.

(U) 1, 1'-Diacetylferrocene

(U) Diacetylferrocene was prepared by the method of Rosenblum and Woodward (Reference 7) which involves Friedel-Crafts condensation of acetyl chloride with ferrocene (65 percent yield).

(U) 1, 1'-bis(carboethoxyacetyl)ferrocene

(U) The procedure of Schlögl, Peterlik and Seiler (Reference 6a) was followed. From 13.3 g (0.049 mole) of diacetylferrocene, 37.3 g of crude disodium salt of the bisketoester was obtained. This was converted to the free bisketoester with cold 1N HCl. Tlc of the crude red oil showed

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a red spot which moved rapidly in ether and a brown stationary spot. The oil was deposited on 50 g of silicar CC-7 (TM) by evaporating a dichloromethane slurry of the oil and the silica gel and chromatographed on 250 g of silicar CC-7 (all Silicar CC-7 was deactivated with 6 percent water). With 10 percent acetone in hexane, an orange band eluted rapidly. A second band eluted more slowly. The desired bisketoester was obtained as a broad band with 25 percent acetone in hexane. Evaporation of the solvent gave a reasonably pure sample, 13.9 g (76 percent yield). The viscous red oil showed no tendency to crystallize.

(U) (U) It was observed that upon standing, the bisketoester slowly decomposed. A simple purification could be accomplished, however, by evaporating a slurry of the oil and florisil (3 g florisil to 1 g oil) in dichloromethane to a red solid. The solid is then washed with anhydrous ether until the washings are colorless. Evaporation of the ether washings leaves the pure bisketoester as a red oil. This procedure was found to be essential prior to the hydrogenation procedure described below.

(U) 1, 1'-bis(β -carboethoxyethyl)ferrocene

(U) This hydrogenation is also described by Schlögl, Peterlik and Seiler as well as others (References 14 and 16b). Considerable difficulty was experienced with hydrogenation of the crude bisketoester. The reaction was very slow even at high pressure and elevated temperatures. It was found that a pure sample of the bisketoester gave much faster reaction. The florisil treatment described above was necessary also if the bisketoester was not freshly prepared. If the PtO_2 catalyst was washed with dilute H_2SO_4 solution as described in "Reagents" (Reference 15) for palladium catalysts, the reaction proceeded even faster. Altogether, the reaction was still quite slow, requiring at least 1 week at 100 psi and 40°C . Extent of the reaction was followed by disappearance of the 6.1μ carbonyl peak in the infrared spectrum. The

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product was isolated as an amber oil and was not purified before proceeding to the next step.

(U) 1, 1'-bis(γ -hydroxypropyl)ferrocene (BHPPF)

(U) A solution 11.4 g (29.5 mmoles) of the crude diester from the hydrogenolysis in 100 ml of dry THF (distilled from LAH and stored over Na) was added dropwise over a 15-minute period to a stirred slurry of 2.24 g (59.0 mmoles) of LAH in 200 ml of dry THF under N_2 . The mixture was refluxed for 1 hour, then cooled and decomposed with 2.25 g of water, 2.24 g of 15 percent KOH solution and 7 g of water (Reference 16). The resulting mixture was filtered and dried over $MgSO_4$. Evaporation of the solvent gave an amber oil which showed only one major spot on tlc. chromatography of the oil on 135 g of Silicar CC-7 (TM) (deactivated with 5 percent water) gave a light yellow band with 10 percent acetone in hexane. The desired diol was eluted shortly thereafter as a broad orange band. Evaporation of the solvent gave a reasonably pure sample as an amber oil weighing 6.3 g (64 percent yield based on 1, 1'-bis(carbo-ethoxyethyl)ferrocene). A pure sample was obtained by molecular distillation; ν_{max}^{plates} 3300, 2800, 1440, 1030 (broad), 925, 905, 820 and 880 cm^{-1} .

Anal: Calcd for $C_{16}H_{22}O_2Fe$: C, 63.6; H, 7.3.

Found: C, 63.2; H, 7.2.

(U) β -Hydroxypropionylferrocene. Attempted Synthesis of 1, 1'-bis-(β -hydroxypropionyl)ferrocene

(U) A solution of 2.16 g (30 mmoles) of β -propiolactone in 25 ml of dichloromethane was slowly added to a stirred slurry of 4.0 g (30 mmoles) of aluminum chloride in 25 ml of dichloromethane under N_2 . Vigorous heat evolution occurred. Only a small amount of undissolved solid remained at the end of addition. To this was added dropwise over a

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30-minute period a solution of 2.0 g (10.7 mmoles) of ferrocene in 25 ml of dichloromethane. The dark purple solution was refluxed 48 hours, then stored at 0°C for 2 days. Ice was added slowly with stirring until heat evolution ceased. The organic phase was separated and dried over MgSO_4 . Tlc showed unreacted ferrocene as a fast-moving spot in 40 percent ether in hexane. A dark red spot moved more slowly and a brown residue did not move. Column chromatography on 50 g of Silicar CC-7 (deactivated with 6 percent water) using 25 percent ether in hexane gave a small amount of unreacted ferrocene. A second band eluted shortly thereafter showed a carbonyl at 6.05μ but no OH absorption. The major constituent was eluted with ether as a dark red band. Evaporation of the solvent gave a deep red oil which was shown to be the monosubstituted product (1.5 g, 54 percent yield). Trituration with hexane gave a solid, m.p. $61-63^\circ$. Recrystallization from petroleum ether ($30-60^\circ$) gave two crystalline forms with identical nuclear magnetic resonance and infrared spectra: yellow needles, m.p. $46-48^\circ$, and red needles, m.p. $64-65^\circ$. $\nu_{\text{max}}^{\text{KBr}}$ 3350, 1645, 1450, 1370, 1260, 1105, 1080, 1055, 1028, 998, and 823 cm^{-1} . $\tau_{\text{TMS}}^{\text{CDCl}_3}$ 5.20 (triplet, 2H, substituted ring protons), 5.49 (triplet, 2H, substituted ring protons), 5.79 (singlet, 5H, unsubstituted ring), 6.00 (triplet, 2H, protons α to carbonyl) and 7.03 (triplet, 3H protons α to OH and OH proton).

Anal. Calcd for $\text{C}_{13}\text{H}_{14}\text{O}_2\text{Fe}$: C, 60.5, H, 5.4,

Found: C, 60.5; H, 5.20.

(U) A second attempt was made to effect disubstitution using 1,2-dichloroethane as solvent. Using the same quantities as in the above experiment and refluxing for 26 hours gave, after workup, a similar mixture of ferrocene and monosubstituted product. Again, there was no evidence of a disubstituted product.

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(U) 1, 1'-bis(β -carbomethoxypropionyl)ferrocene

(U) A sample of this material was prepared by F. M. Dewey by a modification of the procedure of Graham et al. (Reference 8).

(U) 1, 1'-bis(γ -carbomethoxypropyl)ferrocene

(U) Hydrogenation of this bisketoester was identical to that described for 1, 1'-bis(β -carboethoxyethyl)ferrocene except for the starting material.

(U) 1, 1'-bis(δ -hydroxybutyl)ferrocene (BHBF)

(U) A solution of 6.2 g (15.0 mmoles) of the crude bisketoester from the previous step in 50 ml of dry THF was added dropwise to a slurry of 1.9 g (50.0 mmoles) of LAH in 150 ml of dry THF under nitrogen. The mixture was refluxed for 15 minutes. The excess LAH was decomposed with water. The solids were then dissolved by adding 100 ml of 10 percent HCl. Separation gave an orange organic phase which was dried over MgSO_4 and evaporated to a red oil. The crude diol was chromatographed on 200 g of Silicar CC-7 (TM) deactivated with 6 percent water. After a light yellow band, the desired product was eluted as an orange band with 25 percent ether in hexane. Evaporation of the solvent gave 4.2 g (85 percent yield) of the diol as an amber oil. $\nu_{\text{plates max}}$ 3300, 2830, 1430, 1220, 1040 (broad), 1018, 980, 930, 920, 820 and 802 cm^{-1} .

Anal: Calcd for $\text{C}_{18}\text{H}_{26}\text{O}_2\text{Fe}$: C, 65.4; H, 7.86.

Found: C, 65; H, 7.6.

(U) Reduction of 1, 1'-bis(carboethoxyacetyl)ferrocene with LAH and AlCl_3

(U) A solution of 1.003 g (2.41 mmoles) of the bisketoester and 240 mg (1.80 mmoles) of AlCl_3 in 10 ml of dry THF was added dropwise

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to a stirred slurry of 366 mg (9.64 mmoles) of LAH and 480 mg (3.60 mmoles) of AlCl_3 in 10 ml of dry THF. The addition was somewhat exothermic. The reddish-brown suspension was stirred at reflux for 2 hours. After decomposition of the excess LAH and AlCl_3 with water, the mixture was filtered. The organic layer was separated, dried over MgSO_4 and evaporated to a red oil. It showed the presence of carbonyls indicating incomplete reduction. The oil was then treated with the same quantities of LAH and AlCl_3 in the fashion described above for the bisketoester. After stirring at room temperature for 17.5 hours and then refluxing for 5 hours, the mixture was worked up in the same manner. Again, a red oil was obtained (0.6 g) which possessed OH groups but which was free of carbonyls by infrared. This material was chromatographed on 12 g of Silicar CC-7 (TM) deactivated with 6 percent water using 4 percent acetone in hexane. A yellow band eluted rapidly which upon isolation, gave 240 mg of an orange oil, which was tentatively identified as di-n-butylferrocene by comparison of its infrared with that of a known sample.

(U) A second band was then eluted from the column which was evaporated to give a small quantity of a red oil. It showed the presence of OH and methylene groups as well as a ferrocene nucleus. There was insufficient material for purification and further characterization.

(U) A third band was also eluted to give a red-orange oil. The infrared of this material was superimposable with that of a known sample of BHPF.

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| 13. ABSTRACT <p>(C) With the goal of producing a stable, nonmigrating ferrocene burn rate modifier, four ferrocene diols were examined in the role of curing agents. 1,1'-bis(hydroxymethyl)ferrocene and 1,1'-bis(delta-hydroxyethyl)-ferrocene were eliminated because of poor physical properties in the gumstocks and propellants obtained from them. 1,1'-bis(gamma-hydroxypropyl)ferrocene (BHPF) and 1,1'-bis(delta-hydroxybutyl)ferrocene (BHBFB), however, were both found to be excellent curing agents.</p> <p>(C) Both BHPF and BHBFB gave well-cured gumstocks and propellants with the propellant physical properties ranging from 63 to 110 psi tensile strength and 9 to 21 percent elongation. The propellants contained the equivalent of 1.7 to 3.0 percent NBF, but in a form which could not migrate or crystallize, two problems which have plagued NBF.</p> <p>(C) The burn rate enhancement of both diols is at least equal to NBF based on total iron content. Comparisons were made over a range from 0.6 to 1.0 in./s at 1000 psi.</p> <p>alpha gamma delta</p> <p>307 720</p> <p>mk</p> | | | |

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